

Final Technical Report

**Compact Laser-Based Sensors for
Monitoring and Control
of Gas Turbine Combustors**

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1. Abstract

Research is reported on the development of sensors for gas turbine combustor applications that measure real-time gas temperature using near-infrared water vapor absorption and concentration in the combustor exhaust of trace quantities of pollutant NO and CO using mid-infrared absorption. Gas temperature is extracted from the relative absorption strength of two near-infrared transitions of water vapor. From a survey of the water vapor absorption spectrum, two overtone transitions near 1800 nm were selected that can be rapidly scanned in wavelength by injection current tuning a single DFB diode laser. From the ratio of the absorbances on these selected transitions, a path-integrated gas temperature can be extracted in near-real time. Demonstration measurements with this new temperature sensor showed that combustor instabilities could be identified in the power spectrum of the temperature versus time record. These results suggest that this strategy is extremely promising for gas turbine combustor control applications.

Measurements of the concentration of NO and CO in the combustor exhaust are demonstrated with mid-infrared transitions using thermo-electrically cooled, quantum cascade lasers operating near 5.26 and 4.62 μm respectively. Measurements of NO are performed in an insulated exhaust duct of a C_2H_4 -air flame at temperatures of approximately 600 K. CO measurements are performed above a rich H_2 -air flame seeded with CO_2 and cooled with excess N_2 to 1150 K. Using a balanced ratiometric detection technique a sensitivity of 0.36 ppm-m was achieved for NO and 0.21 ppm-m for CO. Comparisons between measured and predicted water-vapor and CO_2 interference are discussed. The mid-infrared laser quantum cascade laser technology is in its infancy; however, these measurements demonstrate the potential for pollutant monitoring in exhaust gases with mid-IR laser absorption.

2. Summary of Results

Significant progress towards the development of TDL sensors for gas-turbine combustors was made during this NASA-funded project. This work focused on gas-fueled combustors, and the results provide the background for liquid-fueled applications.

1. Performed fundamental research in support of real-time laser-absorption temperature sensors
 - a. Near-infrared transitions in water vapor overtones selected with a temperature-sensitive absorbance ratio that can be scanned with a single DFB laser
 - b. Quantitative spectroscopy data acquired in static-cell measurements to enable accurate gas temperature determination
2. Sensor demonstration measurements
 - a. Measurements of gas temperature in a stable laboratory burner validated against thermocouple data
 - b. Rapid (kHz) real-time temperature measurements in a model gas turbine combustor (gas fueled)
3. Real-time software developed
 - a. Real-time gas temperature determination from absorption data
 - b. Real-time identification of acoustic instabilities in laboratory burner

4. Off-site measurement demonstrations
 - a. Measurements at PSI and Stanford using mid-infrared light from quantum cascade lasers to measure trace levels of exhaust CO and NO
 - b. Time resolved near-infrared temperature measurements in the supersonic combustion test rig at Wright Patterson Air Force Base
5. New technology developments
 - a. Fiber-coupled single-laser gas temperature sensor (first use of 1800nm lasers for combustion sensing)
 - b. PLIF measurements of OH to determine individual flame stability in meso-burner array
 - c. Quantum cascade laser sensors developed for measurements of trace amounts of NO and CO in combustor exhaust

3. Publications

1. Xin Zhou, Scott T. Sanders, Jay B. Jeffries, Ronald K. Hanson, and Thomas P. Jenkins, "Combustion Temperature and H₂O Concentration Sensor using a Single Diode Laser," AIAA-2002-0395, 40th Aerospace Sciences Meeting, Reno, NV, January 2002.
2. Shawn Wehe, David Sonnenfroh, Mark Allen, Claire Gmachl, and Federico Capasso, "Measurements of Trace Pollutants in Combustion Flows using Room-Temperature, Mid-IR Quantum Cascade Lasers," AIAA-2002-0824, 40th Aerospace Sciences Meeting, Reno, NV, January 2002.
3. S. Wehe, M. Allen, X. Liu, J.B. Jeffries, and R.K. Hanson, "NO and CO Absorption Measurements with a Mid-IR Quantum Cascade Laser for Engine Exhaust Applications," AIAA-2003-0588, 41th Aerospace Sciences Meeting, Reno, NV, January 2003.
4. X. Zhou, X. Liu, J.B. Jeffries, and R.K. Hanson, "Diode Laser Sensors for Combustion Control," AIAA-2003-1010, 41th Aerospace Sciences Meeting, Reno, NV, January 2003.
5. Xin Zhou, Xiang Liu, Jay B. Jeffries, and Ronald K. Hanson, "Development of a Sensor for Temperature and Water Concentration in Combustion Gases Using a Single Tunable Diode Laser," Measurement Science and Technology, in press.

4. Introduction and Motivation

Advances in gas turbine combustor technology for aeroengine applications are driving combustor designs toward high pressure, ultra-lean operating points. High-pressure operation, up to 50 atm, is desired for improved thrust-to-weight ratio (i.e., a higher energy density heat release) and ultra-lean operation is desired to ameliorate the increase in NO_x and particulate emissions associated with higher-pressure operation. The emissions reduction is also being driven by increasing regulatory pressure to limit NO_x and particulate emissions during all flight phases, not just cruise conditions.

Ultra-lean conditions can move the gas turbine toward stability margin boundaries, resulting in deleterious or potentially destructive combustion instabilities or flame blowoff. Combustor re-light at altitude is also more difficult at ultra-lean conditions, thereby substantially increasing the penalty associated with blow-off. Also,

operating at optimum ultra-lean conditions throughout the power envelope places severe demands on a fixed geometry combustor concept and suggests that adaptive operating modes involving fuel or air distribution may be required to ensure safe and low-emission performance.

For these reasons, there are emerging requirements for sensors, actuators, and control technology suitable in advanced gas turbine combustors. Actuator technology should be capable of modulating fuel and/or air distributions to adapt to changing power demands or alter combustion dynamics to suppress instabilities. Sensors must be able to determine critical combustor and engine operating points such as turbine inlet temperature (T_4), pattern factor, and emission levels. Finally, intelligent closed-loop control systems are required to interpret sensor input and tailor the actuator response to achieve the desired operating conditions.

A basic sensor requirement that may become important in advanced actuator/control schemes is for continuous and real-time measurements of exhaust gas emission of CO and NO at bandwidths of a few Hz. The NO measurement provides for continuous optimization of the engine NO_x emissions while the CO measurement provides for on-line determination of combustion efficiency and serves as a global health monitor diagnostics for fouled fuel and/or injectors. The sensor bandwidth requirement is set by the engine control system response time. Additionally, there are no commercial sensors capable of providing these measurements, and their need has been widely stated, most recently in Reference 1.

Recently, tunable diode-laser absorption sensing was employed for real-time measurement and closed-loop adaptive control of gas temperature and H₂O concentration in the combustion region, CO and hydrocarbons in the exhaust region of laboratory and industrial-scale combustors, and in pulse detonation engines.^{2,3} These measurements are based on near-IR absorption, and an important part of the work reported here, is the development of sensor for such rapid *in situ* measurements of gas temperature using a single, near-IR diode laser.

The near-IR telecommunication diode laser technology probes relatively weak overtone transitions of the target molecules; thus, these wavelengths are a good match for sensors of the primary combustion products water vapor and carbon dioxide, which are present at large concentration in flames. However, sensitive detection of trace CO and NO is generally not feasible at combustion temperatures with near-infrared transitions without resorting to cumbersome and expensive multi-pass cell geometries and drying the exhaust gas. In recognition of this and other applications for ultra-high-sensitivity gas measurements, PSI and Stanford University explored the development of new mid-IR sensor approaches based on room-temperature quantum cascade laser sources operating at 4.6 and 5.4 μm , respectively. Progress toward realization of these sensors is reported here.

5. Research Areas

a. Gas Temperature Sensor

H₂O is one of the primary combustion products and its temperature-dependent absorption spectrum is used here to non-intrusively monitor gas temperature.

Measurements of water vapor are generally relevant to combustion and propulsion engineering, since water vapor concentration can be related to performance parameters such as combustion and propulsion efficiency, and heat release. Tunable semiconductor diode lasers are attractive candidates for absorption measurements of H₂O as these lasers are available at water overtone wavelengths, and are compact, rugged, cost effective, and compatible with optical fiber transmission.

We determine temperature from the ratio of absorption at two different transitions; the ground state number density is related to gas temperature via the Boltzmann population distribution. The emphasis in previous work has been mostly on time-division-multiplexing (TDM) and wavelength-division-multiplexing (WDM) techniques using two diode lasers. Wavelength scanning of a single laser significantly reduces the complexity of these measurements and decreases the potential for interference from beam steering and other broadband losses.

An extensive survey was conducted of near-infrared water vapor spectra and a pair of water vapor transitions near 1800 nm was selected for single-laser temperature measurements in combustion effluent. Fig.1 illustrates the variation in the relative absorption of this line pair simulated by HITEMP.⁴ Note that the absorption lineshape and interference free baseline can be obtained by scanning the laser wavelength less than 0.5 cm⁻¹, a tuning range that a single DFB diode laser can scan at kHz rates. An important part of developing this sensor was the determination of the quantitative spectroscopic parameters. For the line near 1800.45 nm we verified the line position and lines strength data in the HITEMP database and for the line near 1800.57 nm we obtained new data to enable quantitative measurements.

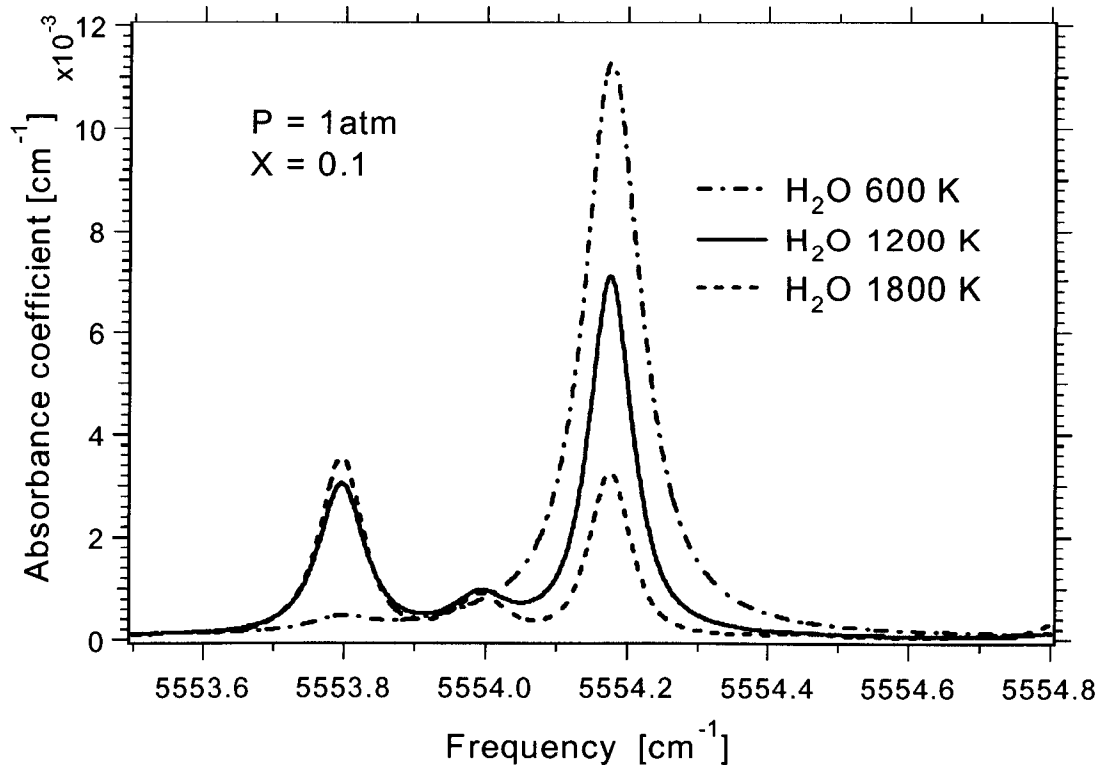


Figure 1. Portion of the H₂O absorption spectrum used for temperature sensing

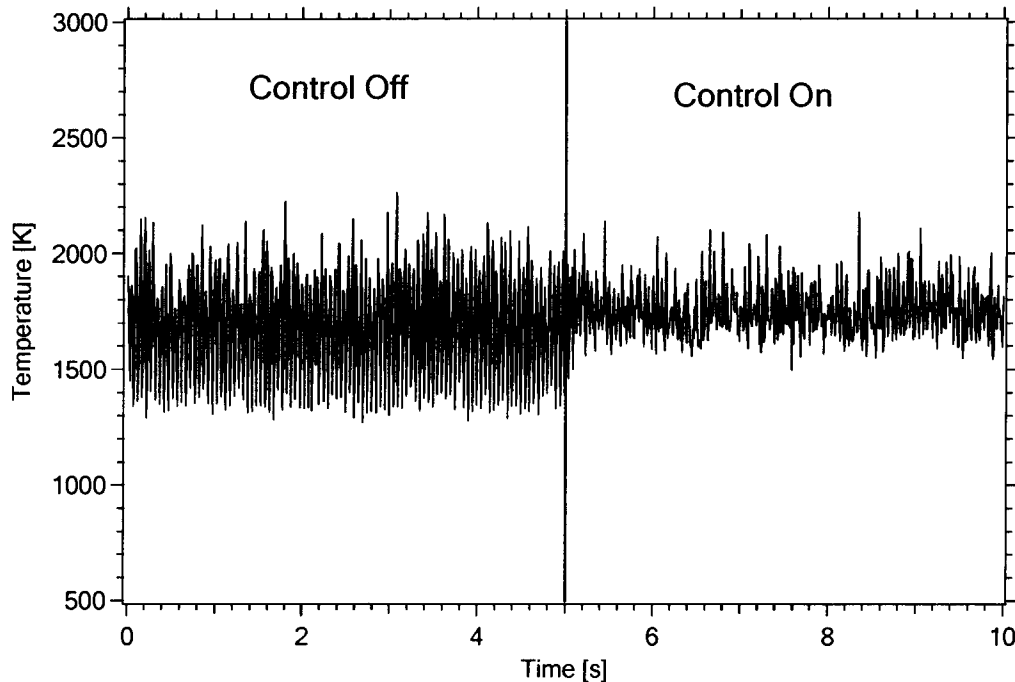


Figure 2. Demonstration of diode laser temperature sensor for closed loop control.

The use of this new sensor for control applications in a small-scale combustor was demonstrated in laboratory measurements. Set-point control of the average gas temperature was performed with closed-loop adjustment of the fuel flow, and an example is shown in Fig. 2 of the temperature fluctuations when the burner is operated open-loop (control off) and closed-loop (control on).

The diode laser sensor was used to make gas temperature measurements in the Stanford University lean direct injection (LDI) gas turbine model combustor. The flame was methane-fueled at an equivalence ratio of 0.66 with a nominal firing rate of 59 kW (Lower Heating Value). The air and methane flows were co-swirled at 45°. The strong swirl produced a typical cone-shaped flame, which was lifted about 0.5" off of the edge of the fuel tube. The flame was mostly confined to the upper half of the 585 mm long combustion chamber. The exit of the chamber transitioned to a 73 mm diameter, 290 mm long "tailpipe" which induced acoustical resonance. Due to the separation of the air and fuel, the flame is primarily a diffusion flame, although there was likely some amount of mixing in the liftoff zone. Characteristic acoustic instabilities are identified from the power spectrum of the temperature time series, as illustrated in Fig. 3. These preliminary experiments demonstrate the feasibility for active combustion control using a single-laser spectroscopic sensing.

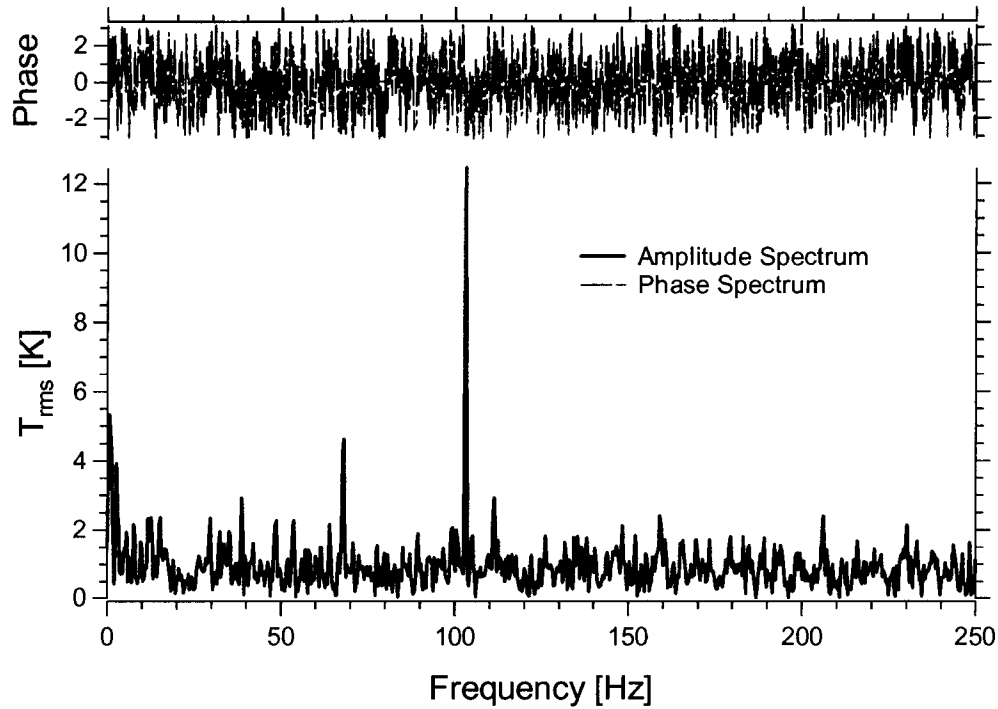


Figure 3. Power spectrum identifies flame instabilities.

b. Aero-Combustor Demonstration of Temperature Sensor

The real-time, near-infrared temperature sensor developed on this grant was demonstrated with measurements in a supersonic combustion test rig at Wright-Patterson Air Force Base during the period September 22 to 27, 2002. The Stanford team consisting of staff engineer Dr. Jay Jeffries and three students (Liu, Zhou, and Lyle) designed, tested at Stanford University, and shipped two diode laser sensor systems to Ohio. After only a single day to unpack and set-up the apparatus, both sensors were successfully used to measure time-resolved gas temperature in post-combustion supersonic flow ($M \sim 2.7$). These results represent the first real-time temperature measurements in a liquid-fueled supersonic combustor and provide an important validation for the utility of diode laser sensors in harsh combustion environments. The rapid deployment of the sensor demonstrates the ruggedness of these diode laser-based sensors. The high quality time-resolved data obtained in the harsh supersonic gas flow demonstrates the potential for real-time diode laser sensing of gas temperature in practical aerocombustors. Leveraging the success of this work, the TDL sensors were modified and applied in pioneering measurements in a gas turbine sector rig at Wright Patterson AFB. These initial tests demonstrate that fiber-coupled TDL sensors can make measurements in the harsh environment of a gas turbine combustor. To our knowledge, this is the first application of TDL sensors in practical-scale gas turbine combustors.

c. Quantum Cascade Lasers

The recent emergence of quantum cascade (QC) lasers enables a new advancement in trace species detection: access to the strong, mid-infrared fundamental vibration-rotation transitions with a room temperature, single-mode, tunable laser. QC

lasers achieve gain via the transitions of electrons between two subbands in the conduction band of a coupled quantum well structure.^{6,7} Inversion is created by engineering the lifetimes of the states involved. The paired electron-injection and active-well regions are replicated many times over (cascaded) to increase output power. Since the transitions occur entirely within the conduction band of the material, the output wavelength is determined by the thickness of the active region and is independent of the band gap. QC lasers can be fabricated at any wavelength from ~ 4.5 to $17\text{ }\mu\text{m}$ using AlInAs/InGaAs lattices on InP. The QC laser design overcomes two main disadvantages of lead salt diode lasers which traditionally are used in this spectral region. First, they can be operated at room temperature, and second, DFB versions can be fabricated to operate in a single longitudinal mode. By accessing the stronger bands in the mid-infrared fingerprint region, a QC laser absorption spectrometer requires a considerably shorter path than a near-IR device of comparable sensitivity. These advantages result in an overall sensor system that will be smaller and less complex than existing lead salt or near-IR sensors. Thus, the advent of QC lasers enables a new generation of laser-based sensors which achieve the sensitivities of lead salt laser sensors and incorporate the robustness and ease of operation of near-IR diode laser sensors.

Several groups have recently reported applications of QC lasers to trace gas sensing. Sensitive absorption spectroscopy using frequency modulation (FM) detection and a room temperature, pulsed DFB QC laser has been reported.⁵ Sensitive absorption spectroscopy has also been demonstrated with cryogenically cooled, CW QC lasers using either FM detection⁶ or photoacoustic detection techniques.⁷ Detection of isotopic composition has also been demonstrated using cryogenically cooled, CW QC lasers.⁸

Our work focuses on quasi-CW, room temperature operation of the laser source with high sensitivity detection achieved using the balanced ratiometric technique. We have demonstrated the operation of a breadboard QC laser system to detect N_2O and NO near $5.4\text{ }\mu\text{m}$,⁹ and are currently developing a number of related sensors. While QC lasers can be operated CW at cryogenic conditions, we take the approach of pulsed operation at thermoelectrically cooled conditions near room temperature. The noise reduction techniques include (1) reduction of thermal noise through use of liquid-nitrogen-cooled field of view, and (2) dual-beam, balanced ratiometric detection (BRD).^{10,11}

d. Experimental Configurations for Quantum Cascade Laser Measurements

To simulate the gas turbine exhaust environment for sensor development, absorption measurements of the target species, NO and CO should be performed at 800K , and in the presence of major combustion products (CO_2 and H_2O). However, these conditions are difficult to achieve in a laboratory setting required for sensor development. The approach taken to date, has been to operate a flat-flame burner near the flammability limits to achieve the coolest flame products as possible. An optical path is then folded above the burner to provide an appropriate pathlength. For the CO measurements, trials using different reactant gas combinations were used with the goal of achieving a stable cool flame with ppm levels of CO . A rich hydrogen-air flame at an overall equivalence ratio of 2.5 was developed at 1150 K . Excess nitrogen was added to the *air flow* to cool

the flame temperature. Dissociation of added CO₂ to the burner supply gas was used to seed the flow with CO.

A facility developed at Stanford University also uses a flat-flame burner but its exhaust is routed into a horizontal duct to form a cool (with respect to the flame temperature) stable region with good optical access. Modifications to the facility, which permitted safe operation as high as 600 K, were recently completed and NO measurements were performed in the exhaust of an ethylene-air flame containing all of the appropriate combustion products.

i. McKenna Burner Measurement Description

Figure 4 depicts the experimental schematic for the QCL based combustion-gas exhaust measurements of NO taken at Stanford University. The combustion test facility located in the bottom of Fig. 4 consisted of a water-cooled atmospheric pressure ethylene (C₂H₄) - air premixed flat-flame (McKenna) burner¹² (6 cm diameter), a vertical exhaust stack and a 122 cm long horizontal-insulated duct 76 cm above the burner. The insulation permits a uniform temperature distribution across the length of the duct. C₂H₄ and dry-air flows were metered with calibrated rotameters, premixed and injected into the burner. A fixed dry-air flow rate (30 L/min) was used with varying fuel flow rates (1.49 to 3.25 L/min) to adjust the equivalence ratio over a range of 0.71 to 1.55. Uncertainty in the fuel flow rate, and thus the equivalence ratio, was estimated to be approximately $\pm 2\%$. NO was injected into the vertical exhaust stack using a flush port located 18 cm above the burner surface. The transverse temperature profile of the horizontal exhaust stack was measured using three thermocouples (Type-K, bead size of 0.04 in.) which were distributed along the duct.

The top portion of Fig. 4 illustrates the optical arrangement used in the NO measurements. A QC laser (shown near the top) is mounted inside a purged laser mount pictured in Fig. 5. The QCL mount contains a two-stage thermo-electric cooler (TEC) to control the laser temperature (-30 to 40°C) and thus coarsely control the laser wavelength. The method of supplying current pulses to the QCL involves the use of a pulsed current source (capacitive discharge) with fixed pulsed amplitude (up to 7 A/pulse) at 1.5 MHz repetition rate. The pulses are combined in a bias-tee network with a slowly varying sub-threshold current ramp (approximately 100 mA). The two current waveforms are added together to provide the laser with high amplitude current pulse for lasing and a sub-threshold current for tuning ($\sim 1 \text{ cm}^{-1}/\text{sweep}$) via joule heating. Pulse widths approximately 5 to 10 ns wide (FWHM) are achieved using an integral pulse driver (printed circuit board) mounted directly inside the laser housing (see Fig. 5).

The laser emission is collimated using an AR coated f/1 ZnSe lens (installed in a five-axis mount) and directed onto a pellicle beam splitter. The nitrocellulose pellicle was selected to minimize the contribution of fringes associated with conventional beam splitters. A HeNe laser is co-aligned with the IR beam and is used for coarse IR-beam alignment through the exhaust stack. Approximately 30% of the power is directed into the exhaust stack via a pair of gold steering mirrors, while the remainder is collected on an LN₂-cooled InSb reference detector (equipped with a cold field of view) using an off-axis-parabolic mirror (OAP). The windows on the exhaust-stack entrance and exit ports

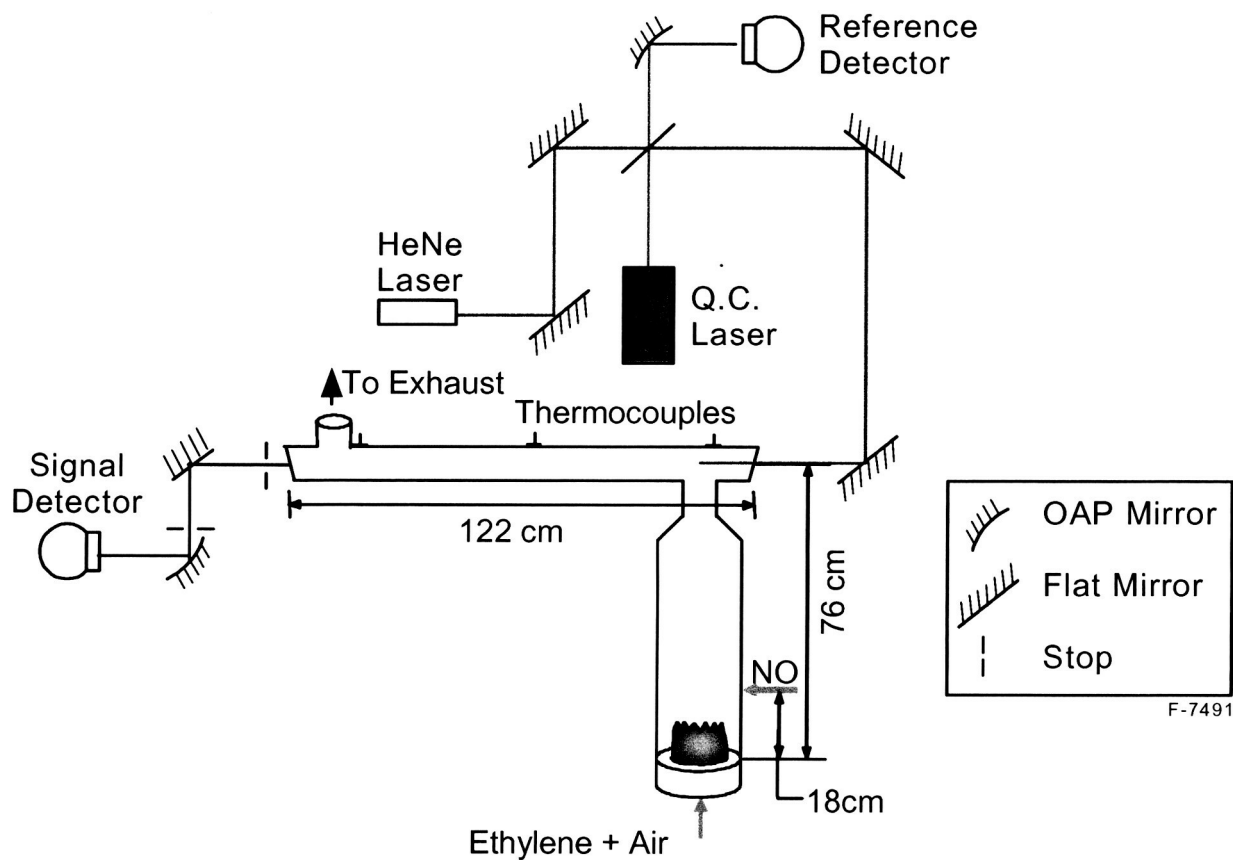


Figure 4. A schematic of the experimental setup used to examine QC laser absorption in the exhaust of a premixed ethylene-air flame.

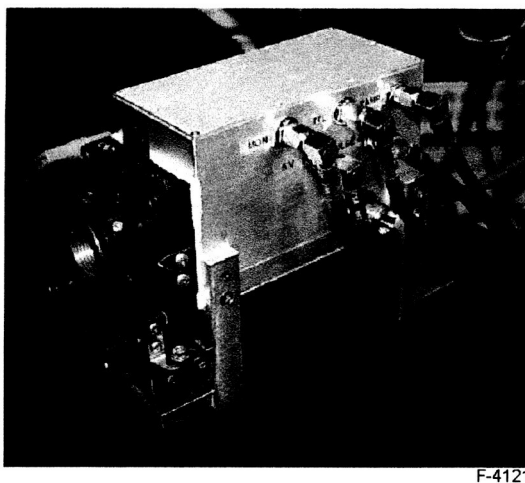


Figure 5. Photo of the QCL mount.

are 3 deg wedged CaF_2 uncoated windows. The wedge angle was selected to minimize the effect of fringes generated from the window surfaces. Beam stops are aligned along the exhaust-stack exit path leading to the signal detector to reduce the collection of background radiation. A solid germanium etalon (free-spectral range 1.67 GHz) was employed to determine the relative frequency variations during the laser tuning.

ii. Hencken Burner Measurement Description

Figure 6 depicts the experimental schematic for the CO flat-flame burner absorption measurements taken at PSI. From the bottom, a gas handling system provides metered flows of fuel and oxidizer to a Hencken-type flat-flame burner. This burner uses a dense array of diffusion flamelets which merge within 1 mm of the honeycomb surface to form a well-characterized gas flow that achieves near-equilibrium conditions for major species and over a range of fuel-oxidizer stoichiometries and temperatures. Flows of the various gases were delivered to the burner using commercial mass-flow meters and precision needle valves.

For the CO experiments, the output of a QC laser is processed similarly as shown in the top of Fig. 4. However, in this configuration the stronger of the split beams (60% power) is directed to the multi-pass cell (MPC) via a pair of steering mirrors. This portion of the optical train is shown in Fig. 6. More power is directed to the signal detector to compensate for losses encountered from a grating (150 mm^{-1}). The grating is used to reduce the collection of background emission from the flame before collection on the signal-detector. Additionally, the electrical current addition concept (short pulse plus slowly varying ramp), described for the NO measurements, is similar to the one employed in the CO measurements. The pulse frequency was 950 kHz in these measurements and the frequency of the scan was 100 Hz. The pulser in these experiments is commercially available from Agilent and the bias-T network is located external to the QCL mount.

Figure 7 illustrates the MPC and burner geometry used for the CO measurements. The cell is constructed of two 5-cm diameter, $f/2$ gold spherical mirrors with inlet and outlet holes. The waist of the IR beam is fixed in the center of the MPC. Nine passes across the burner surface were achieved with this mirror set, and a beam diameter of approximately 4 mm. The resulting pathlength in the flame is 23 cm.

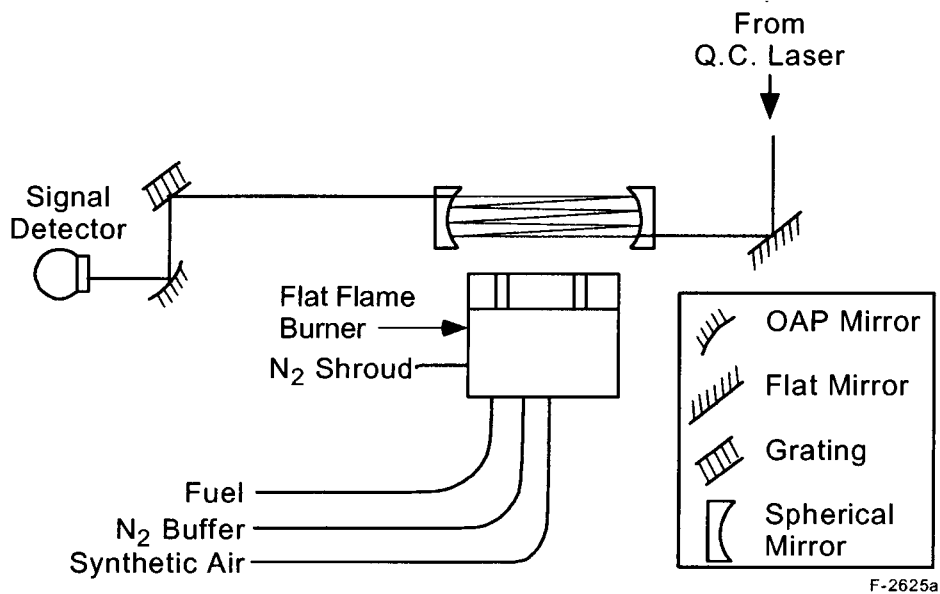


Figure 6. A schematic of the experimental setup used to examine CO absorption in flames.

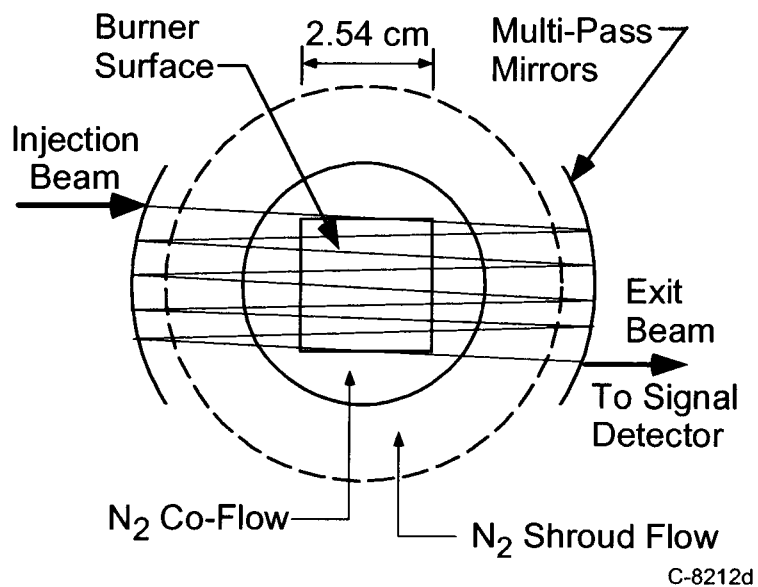


Figure 7. Experimental schematic of the PSI flat-flame burner measurements.

e. Mid-IR Measurements with Quantum Cascade Lasers

Although strong fundamental transitions are available for both CO and NO in the mid-IR, the presence of water vapor and carbon dioxide present potential difficulties in obtaining low detection limits. The interference from these species is a primary issue that our work sought to address. In the past the HITRAN and HITEMP databases have been used to simulate the absorption spectra of typical engine exhaust conditions (800 K) however earlier measurements which were at higher temperatures suggested that the measured baseline was easier to determine than predicted.

i. Spectral Survey of the NO $R_{(6,5)}$ Line

The results of earlier measurements show that the $R_{(6,5)}$ line is a potential candidate for high-sensitivity measurements of NO in the presence of water vapor.¹³ Figure 8 shows the results of a spectral survey surrounding the $R_{(6,5)}$ line of NO in the presence of water vapor and CO₂. The top-most portion of the figure shows a Hitran/HITEMP (CO₂, NO, and H₂O) simulation at 600 K and for $X_{NO} = 50$ ppm, $X_{CO_2} = 10\%$, and $X_{H_2O} = 10\%$. The bottom portion shows measurement near 1900 cm⁻¹ from the exhaust of an ethylene flame at an equivalence ratio of 1.04 with and without seeding of nitric oxide. The difference between the two spectra, shown in the middle portion, depicts the resulting signal generated solely from NO absorption. The doublet spacing confirms the identification of the correct NO transition. Furthermore, the nearby features observed due to CO₂ and H₂O are clearly identified.

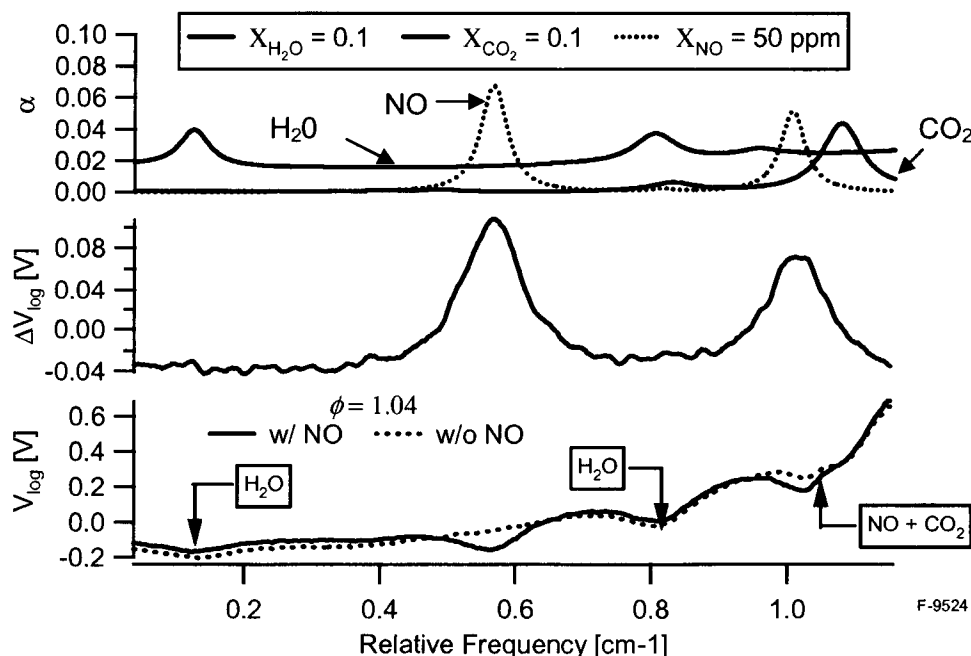


Figure 8. A spectral absorption survey of NO over the $R_{(6,5)}$ transition near 1900 cm⁻¹.

From these results one can see the NO signal can be distinguished from water vapor and CO₂. It is also observed that the lineshape is broader than that predicted by the

broadening parameters available in HITRAN. The dominant contribution to the discrepancy between the predicted and measured widths is due to spectral chirp associated with joule heating during the pulse event, and we estimate the width to be approximately 1.5 GHz. Instantaneous widths of the QC lasers are approximately 1 MHz,¹⁴ and a few kHz¹⁵ when frequency stabilized feedback loops are used in the current source. The remaining contribution to the discrepancy in width is due to the lack of collisional-broadening data included in the HITRAN model.⁴

Figure 9 shows a series of lineshapes acquired for NO as in Fig. 7, but with the spectral scan range limited to the strong $R_{(6,5)}$ feature. A range of seeding levels were examined at an equivalence ratio of 1.04, an exhaust-gas temperature of approximately 609 K, and a pathlength of 1.2 meters. The lineshapes are acquired at a 100-Hz rate and digitally filtered at 1.5 kHz. The absorbance is calculated from the log output of the BRD electronic circuit which was calibrated using direct absorbance measurements. Thus, these absorbance measurements include the instrument width of the laser.

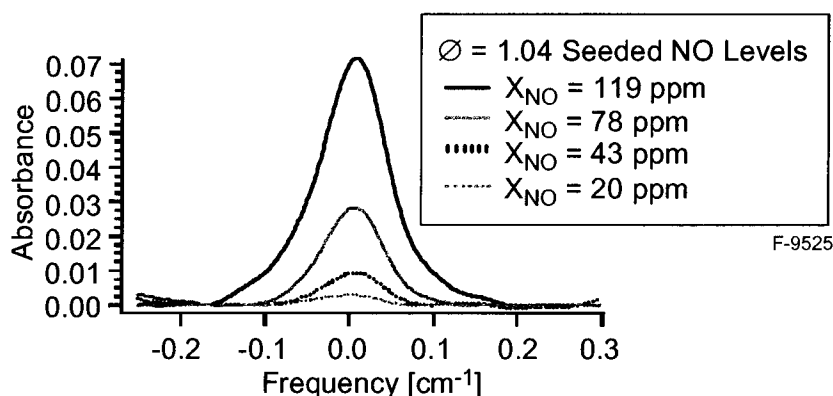


Figure 9. Measured absorption lineshapes ($R_{(6,5)}$ at 1900.1 cm^{-1}) in a C_2H_4 +air flame at an equivalence ratio of 1.04 over a range of seeding levels.

The noise in these spectra corresponds to an equivalent detection limit of approximately 0.30 ppm and represents an equivalent absorption (fractional change in the transmitted laser intensity) of about 4×10^{-4} . This sensitivity is approximately two orders of magnitude less than those typically achieved with near-IR CW TDL sensors using BRD methods. The reduction in sensitivity is attributed to radiation from the exhaust duct impinging on the signal detector, and a relatively low-duty-cycle pulsed-current waveform. The sensitivity of this measurement extrapolated to 800 K (typical of gas turbine exhaust temperatures) and a 1-m pathlength corresponds to a sensitivity of 0.66 ppm-m. However, a reduction in the laser's spectral width would recover approximately a factor of 2 in sensitivity.

Figure 10 shows the measured NO fraction in the exhaust gas versus the seeded level determined using rotameter measurements in the supply gases. The measured concentration was determined by integrating the area under the absorbance measurements and using the sum tabulated in HITRAN which exist in a tight band near 1900.075 cm^{-1} . These results illustrate that the NO chemistry was not frozen, even at these low-temperature conditions. However, flow modeling results using Chemkin predict that NO

is frozen for both $\phi = 0.71$ and $\phi = 1.04$ over a temperature range of 617 to 730 K, but wall-catalyzed NO to NO₂ conversion effluent is possible. To address this issue, extractive sampling measurements using a chemiluminescent analyzer are underway.

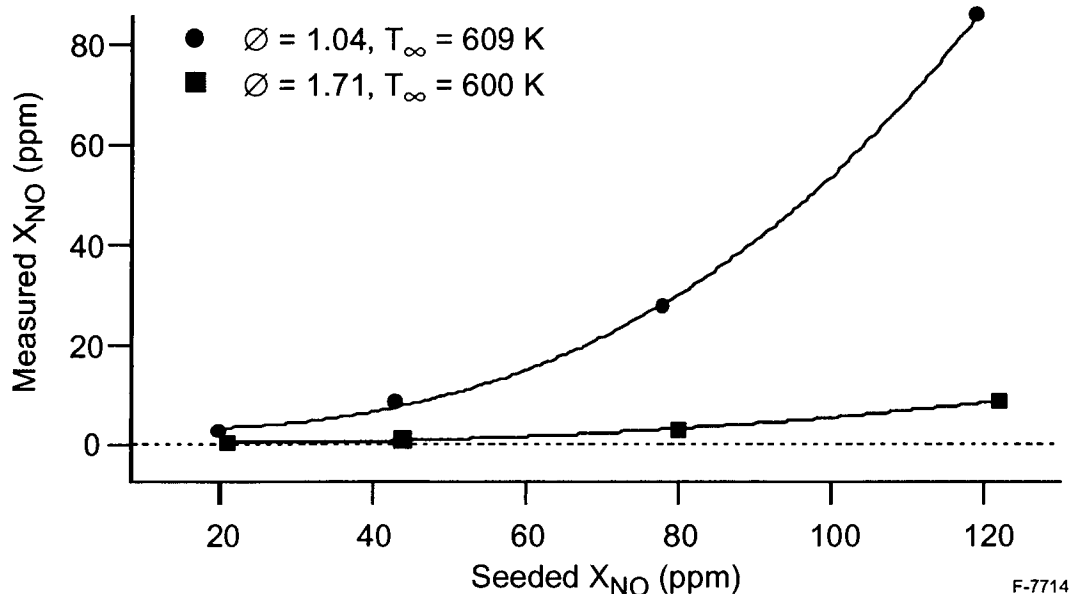


Figure 10. Results of an NO absorption measurement in a, $\phi = 0.71$ and 1.04 ethylene-air flame.

ii. Spectral Survey of the CO R₍₅₎ Line

Spectral simulations using the HITRAN data base show that the R₍₅₎ line is a candidate transition for a CO sensor. Figure 11 shows example absorption lineshapes of the R₍₅₎ CO transition recorded in a 23-cm folded path directly above a Hencken-type flat-flame burner. The burner was operated at approximately 1150 K (as measured with a thermocouple) using H₂-Air diluted with excess N₂ to reduce the flame temperature. Trace amounts of CO were produced in the flame from dissociation of CO₂. In the top left of the figure the measured concentration is shown compared to the equilibrium concentration calculated using an equilibrium solver (StanJan). The burner was operating very close to its lean blow-off limit and, especially at these low combustion temperatures, it is not particularly surprising that the combustion gases are not in full equilibrium. A calculated CO lineshape for a CO concentration of 27 ppm in a 1.2 m pathlength is also shown in Fig. 11. In this figure the absorbance axis for the calculated spectrum is shown on the right-hand axis. This lineshape illustrates the instrument broadening associated with the laser.

The noise equivalent absorbance is 5×10^{-5} , corresponding to a detection limit of 0.21 ppm-m at 1150 K. Extrapolating the sensitivity to 800 K (the temperature of a typical gas turbine exhaust), the sensitivity is 0.10 ppm-m. The improvement in NEA compared to the NO measurements is attributed to use of a grating which reduces the collection of background radiation.

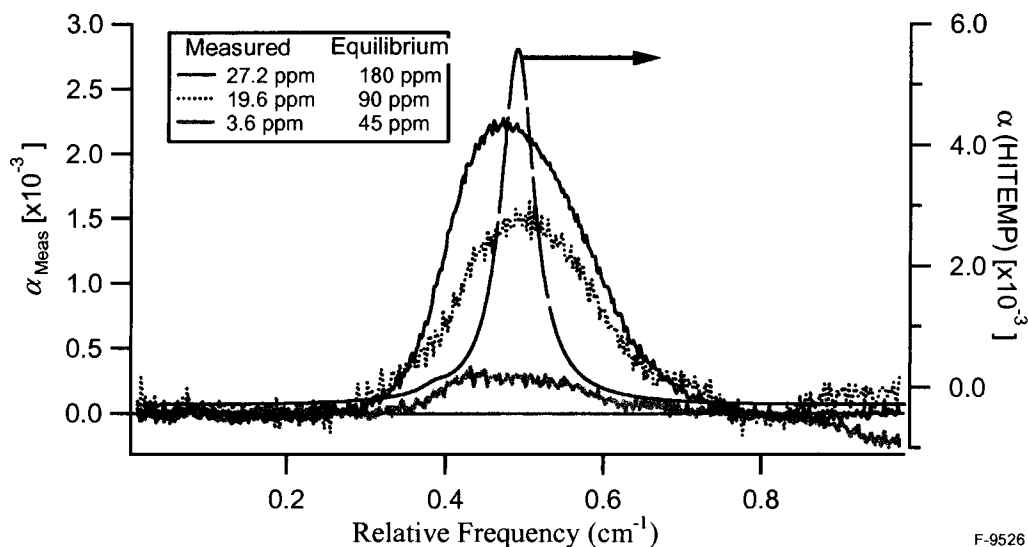


Figure 11. Measurements of CO absorbance ($R_{(5)}$ at 2165.6 cm^{-1}) in a $\text{H}_2 + \text{Air} + \text{N}_2 + \text{CO}_2$ Flame are presented. The flame temperature is 1153 K at an overall equivalence ratio of 2.5.

f. Mid-IR NO and CO Sensor Potential

The results of room-temperature mid-IR Quantum Cascade Laser measurements of CO and NO demonstrate promise for sensitive, in-situ measurements of the trace combustion-generated species. The extractive sampling results are needed to provide accurate measurements for direct comparison and to refine the experimental apparatus. The results of the NO measurements, which were performed in the presence of the expected interfering species, CO_2 and H_2O , demonstrated that the absorption signal was clearly distinguished from the background. Therefore, this transition is a good candidate for NO-sensor development. The CO measurements were also measured with water vapor as a potential interfering species, and the indications are it is a good candidate for combustion applications. Further work investigating potential CO_2 interference is recommended.

Sensor development will benefit from enhancements in QCL pulser technology. The results illustrate that measured spectral widths of CO and NO are wider than predicted. A laser spectral width on par with NIR diode lasers would yield a factor ≥ 2 in sensitivity as the absorbance signal will increase relative to the background. A reduction in instrument width can be achieved by reducing the pulse width up to the point that the transform limit width exceeds the chirp width (estimated to be approximately 600 MHz). Pulser development is on-going which will reduce the pulse width (which is currently estimated to be 5 to 10 ns wide) and increase the pulse currents to surpass the threshold currents of commercially available QC lasers. Demonstrations of a reduced laser linewidth will be made on a purely Doppler-broadened lineshape to permit quantitative determination of the laser linewidth.

Finally, further development of a sensor requires improved methods for isolating the target transition from neighboring interferences. The spectral range of the QCL is sufficient to measure neighboring isolated CO_2 and H_2O transitions as demonstrated in

the 1.2 cm^{-1} survey of NO. Thus, spectral modeling based on measured water and CO₂ spectra at relevant temperatures could be used to determine a baseline. Spectra of the major interfering species can be obtained using the exhaust from a hydrogen+O₂ flame (appropriately diluted with Ar) along with separate measurements using a CO+O₂ flame in the Stanford burner. The results of the measured interfering species could be incorporated into a spectral model to provide a calculated baseline for subtraction from the target species' measured spectrum.

6. References

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